

The Crystal Structure of $K_2[B_5O_8(OH)] \cdot 2H_2O$

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$K_2[B_5O_8(OH)] \cdot 2H_2O$ crystallizes in the orthorhombic system with lattice parameters $a = 12.566 \pm 0.005$ Å, $b = 6.671 \pm 0.003$ Å and $c = 11.587 \pm 0.005$ Å in space group $Pna2_1$. There are four molecular formulas per unit cell. The structure was solved by the Zachariasen statistical method and three-dimensional Patterson and Fourier series. The positional and anisotropic thermal parameters have been refined by the least-squares method based on 1440 structure factors. The final conventional R index is 0.044.

The structure contains units $[B_5O_8(OH)]^{2-}$ constructed from two BO_4 tetrahedra, two BO_3 triangles and one $BO_2(OH)$ triangle by sharing corners. Each polyion shares four of its oxygen atoms with four different units. In addition, they are held together by hydrogen bonds and K–O bonds. This array of oxygen–boron and oxygen–potassium polyhedra forms empty channels parallel to the b axis, in which the two water molecules of hydration are accommodated. The mean bond lengths are K–O (eightfold coordination) = 2.805, B–O (threefold coordination) = 1.370, B–O (fourfold coordination) = 1.483, H–O = 0.96, $H \cdots O = 2.18$ Å.

The unique position of these water molecules, and their weak hydrogen bonding with the rest of the structure, seem to indicate that $K_2[B_5O_8(OH)] \cdot 2H_2O$ can lose the waters of hydration without changing structure. These findings corroborate the predictions about the zeolitic nature of the hydration water made from thermogravimetric studies.

Introduction

The author began the determination of the crystal structure of $K_2[B_5O_8(OH)] \cdot 2H_2O$ in 1962 while working with W. H. Zachariasen at the University of Chicago. Professor Zachariasen has had a continuing interest in borate structures since the nineteen thirties.

The polyborate $K_2[B_5O_8(OH)] \cdot 2H_2O$ was prepared for the first time by Auger (1925). The first single crystals were prepared by Carpéni and his collaborators. (Carpéni, 1954; Carpéni, Haladjian & Pilard, 1960). These authors studied the dehydration-hydration process of $K_2[B_5O_8(OH)] \cdot 2H_2O$. They found that this salt can lose or regain reversibly two molecules of water per molecule of salt. However, if the dehydration is carried on any further, the product obtained, $K_4B_{10}O_{17}$, cannot be hydrated back to $K_2[B_5O_8(OH)] \cdot 2H_2O$. This was interpreted by Carpéni *et al.* as an indication that the two waters of hydration are of zeolitic nature and that the hydroxyl group is essential to the structure of the polyborate $K_2[B_5O_8(OH)] \cdot 2H_2O$.

This paper reports the results of a detailed structural study of the polyborate $K_2[B_5O_8(OH)] \cdot 2H_2O$.

Crystal data

The crystals used in this investigation were kindly supplied by Professor G. Carpéni. The symmetry, the space group and approximate lattice parameters were determined from Weissenberg and precession photographs taken with Cu $K\alpha$ and Mo $K\alpha$ radiation, respectively. The crystals of $K_2[B_5O_8(OH)] \cdot 2H_2O$ were found to be orthorhombic with 4 molecules per unit

cell of dimensions $a = 12.566 \pm 0.005$, $b = 6.671 \pm 0.003$, and $c = 11.587 \pm 0.005$ Å. The calculated density is 2.142 g.cm⁻³ as compared with the measured value of 2.15 g.cm⁻³ given by Carpéni, Haladjian & Pilard (1960). The lattice parameters were determined from the scattering angles of 12 reflections with large 2θ values, as measured by a single crystal General Electric diffractometer and Cu $K\alpha$ radiation. The final values were calculated by the use of the least-squares method. The systematic absences are $0kl$ for $k+l = 2n+1$ and $h0l$ for $h = 2n+1$. These absences correspond to two space groups, $Pna2_1$ and $Pnam$. A piezoelectric test was made on the crystal of $K_2[B_5O_8(OH)] \cdot 2H_2O$ with a sensitive Giebe–Scheibe apparatus and found negative, although the Patterson function (see solution of the structure) indicated that the correct choice of space group is $Pna2_1$. All atoms are in the general positions

$$(x, y, z; \bar{x}, \bar{y}, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - y, z).$$

Experimental

The intensity measurements were made with a General Electric automatic diffractometer, with the use of Zr-filtered Mo K radiation and a scintillation counter. The specimen was a crystal with a prismatic habit, the longest direction being ~ 0.25 mm. This crystal was oriented with $[010]$ zone axis parallel to the φ axis of the goniostat. The integrated intensities were obtained with the stationary-crystal stationary-counter technique and single filter. The take-off angle was 8° . The background was measured on each side of the peak at

2° off the peak itself and the average was subtracted from the peak height. All reflections included within an octant in reciprocal space having $2\theta \leq 90^\circ$ were measured. The total number of independent reflections measured was 4334. Those reflections for which the peak height was not at least twice as much as the background were regarded as unobserved. This criterion gave 1478 observed reflections and 2856 unobserved. The integrated intensities were converted to structure factors using a computer program written by Prewitt (1966). No absorption correction was applied since the dimensions of the crystal were such that the absorption effect was negligible.

Solution of the structure

The first step for solving the structure of $K_2[B_5O_8(OH)] \cdot 2H_2O$ was based on calculating a three-dimensional Patterson synthesis which was carried out by the use of the program 'Four' written by Fritchie (1967) and modified by L. Guggenberger and by P. B. Jamieson. The squares of the 1478 observed structure factors on an arbitrary scale were the input vectors. The concentration of vectors of the sections $xy\frac{1}{2}$, $x\frac{1}{2}z$ and $\frac{1}{2}yz$ indicated that the correct space group was $Pna2_1$. According to this space group symmetry the xy projection of the structure has a center of symmetry. By the statistical method introduced by Zachariasen (1952) a self-consistent set of signs for 33 strong F_{hko} terms was deduced. A Fourier synthesis carried out with these terms gave the approximate x and y coordinates of the two potassium atoms; K(1) ($x_1=0.044$, $y_1=0.14$) and K(2) ($x_2=0.25$, $y_2=0.50$). In addition, most of the strongest peaks in the Patterson synthesis could be explained by placing K(1) at 0.044, 0.144, 0.00; and K(2) at 0.252, 0.498, 0.191. Structure factors based on these coordinates, assuming isotropic temperature factors of 0.4 \AA^2 yielded $R = \Sigma |\Delta F| / \Sigma |F_o| = 0.4$. A three-dimensional Fourier synthesis, computed with the signs of the two potassium atoms, gave the positions of the 11 oxygen and 5 boron atoms. The positions of these atoms, those of the potassium atoms, and the isotropic temperature factors were subsequently refined by the program *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The f -curves for neutral atoms of K, O, and B given by Cromer & Waber (1965) were used. All observed structure factors were weighted equally with the exception

of those reflections for which $\frac{\sin \theta}{\lambda} \leq 0.20$. Because

of the high background errors for these reflections, zero weight was assigned to the corresponding structure factors. This criterion reduced the number of reflections on which the refinement was based to 1440. Convergence was attained after three cycles and reduced the R index to 0.095. A three-dimensional difference Fourier showed a number of small peaks. The number of these peaks was greater than the number of

hydrogen atoms present in the unit cell, indicating that some peaks were spurious. The starting positions for the 5 hydrogen atoms were chosen by taking into account the difference Fourier synthesis and the structural arrangement obtained from the preliminary refinements. For instance, the short O(8)–O(5) distance could be explained only in terms of an O–H...O bond, and since O(10) and O(11) are not bonded to any boron, these oxygens should belong to the water molecules.

The final refinement provided for the simultaneous adjustment of 177 parameters: 1 scale factor, 68 position parameters and 108 thermal parameters. Anisotropy was assumed for the thermal motion of potassium boron and oxygen atoms, while an isotropic thermal factor $B=5.0 \text{ \AA}^2$ was postulated for the hydrogen atoms. In this last refinement each observed structure

factor with $\frac{\sin \theta}{\lambda} \geq 0.2$ was weighted by $w=1/\sigma^2$

where $\sigma=2$ when $|F| \leq 20$ and $\sigma=0.1|F|$ when $|F| > 20$.

The results of the final refinement, which gave $R=0.044$ and $wR = [\Sigma (w^{1/2}\Delta F)^2 / \Sigma (w^{1/2}F_o)^2]^{1/2} = 0.058$ are shown in Tables 1 and 2, while Table 3 shows the degree of agreement between observed and calculated structure factors.

Table 1. Final positional parameters

	x	y	z
K(1)	0.0432 (1)	0.1431 (2)	0.0
K(2)	0.2495 (1)	0.4978 (2)	0.1902 (2)
B(1)	0.2906 (4)	0.9945 (7)	0.0285 (4)
B(2)	0.1624 (4)	0.1613 (6)	0.4373 (4)
B(3)	0.0209 (4)	0.3879 (7)	0.5138 (5)
B(4)	0.2204 (4)	0.0433 (7)	0.2405 (4)
B(5)	0.2785 (4)	0.3096 (7)	0.8992 (4)
O(1)	0.4063 (3)	0.0219 (5)	0.0542 (3)
O(2)	0.2281 (3)	0.0810 (5)	0.1252 (3)
O(3)	0.1785 (3)	0.1865 (5)	0.3103 (3)
O(4)	0.0486 (3)	0.2145 (5)	0.4588 (3)
O(5)	0.2334 (2)	0.2848 (4)	0.5063 (3)
O(6)	0.2605 (3)	0.1157 (4)	0.9249 (3)
O(7)	0.3243 (3)	0.4472 (4)	0.9690 (3)
O(8)	0.4154 (3)	0.0620 (7)	0.5292 (5)
O(9)	0.2443 (3)	0.3634 (5)	0.7873 (3)
O(10)	0.4474 (5)	0.3132 (1)	0.2236 (5)
O(11)	0.0089 (8)	0.2506 (3)	0.7729 (9)
H(1)	0.36 (2)	0.15 (3)	0.53 (2)
H(2)	0.44 (2)	0.20 (3)	0.19 (2)
H(3)	0.51 (2)	0.25 (3)	0.27 (2)
H(4)	0.43 (2)	0.79 (3)	0.24 (2)
H(5)	0.53 (2)	0.63 (3)	0.21 (2)

Description and discussion of the structure

The results of the final refinement give the interatomic distances reported in Table 4. Their values with the standard deviations were calculated by the use of Busing, Martin & Levy's (1964) *ORFFE* program.

Fig. 1 shows a projection of the structure of $K_2[B_5O_8(OH)] \cdot 2H_2O$ on the XZ plane. The structure contains the units $[B_5O_8(OH)]^{2-}$ which consist of a central BO_4 tetrahedron with two opposite tetrahedral edges shared with a B_2O_5 group on one side and a

$B_2O_5(OH)$ group on the other. A projection of the unit on the (101) plane is shown in Fig. 2. The group B_2O_5 consists of two boron–oxygen triangles, whereas the

group $B_2O_5(OH)$ consists of one boron–oxygen tetrahedron and one boron–oxygen triangle. The unshared oxygen of this triangle is a hydroxyl group. Each unit

Table 2. Anisotropic thermal parameters*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			($\times 10^4$)			
K(1)	20 (1)	84 (2)	53 (1)	-5 (1)	-8 (1)	4 (1)
K(2)	58 (1)	58 (1)	17 (1)	-12 (1)	6 (1)	-2 (1)
B(1)	13 (2)	36 (6)	10 (2)	5 (3)	1 (2)	3 (3)
B(2)	15 (2)	25 (6)	9 (2)	6 (3)	14 (2)	15 (4)
B(3)	12 (2)	47 (7)	25 (3)	0 (3)	8 (2)	-11 (4)
B(4)	13 (2)	36 (6)	15 (2)	0 (3)	-2 (2)	2 (3)
B(5)	16 (2)	42 (7)	10 (2)	-8 (3)	3 (2)	5 (3)
O(1)	14 (2)	58 (6)	30 (2)	2 (2)	-3 (2)	-14 (3)
O(2)	23 (2)	57 (5)	7 (1)	8 (2)	5 (1)	-2 (2)
O(3)	32 (2)	39 (5)	9 (2)	9 (3)	0 (2)	0 (2)
O(4)	13 (2)	62 (5)	30 (2)	6 (3)	0 (2)	-18 (3)
O(5)	14 (1)	39 (4)	16 (2)	4 (2)	0 (1)	-3 (2)
O(6)	23 (2)	35 (4)	11 (2)	-1 (2)	1 (1)	4 (2)
O(7)	18 (2)	34 (4)	14 (2)	-1 (2)	-4 (1)	2 (2)
O(8)	16 (2)	110 (9)	86 (5)	4 (3)	8 (2)	56 (5)
O(9)	40 (2)	59 (5)	13 (2)	-21 (3)	-10 (2)	9 (3)
O(10)	56 (3)	199 (15)	47 (4)	13 (6)	-22 (3)	23 (6)
O(11)	79 (7)	661 (40)	92 (7)	-37 (14)	-3 (6)	107 (15)

* The anisotropic thermal parameters are the coefficients in the expression
 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

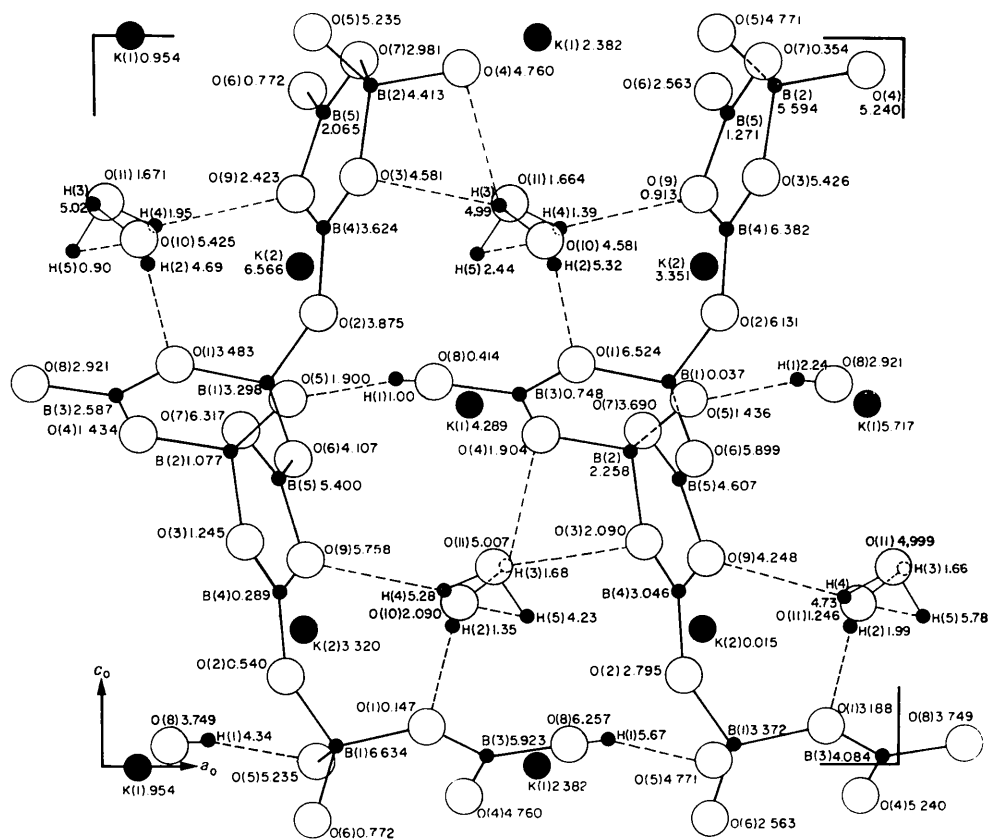


Fig. 1. The projection of one unit cell on the XZ plane. The heights of the atoms are in ångströms. Note that a left handed system of axes has been used.

Table 3. Comparison of observed and calculated structure factors

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
2	0	0	106.1	87.0																									
4	0	0	193.6	136.9																									
6	0	0	104.7	100.8																									
8	0	0	61.1	61.1																									
10	0	0	17.2	17.2																									
12	0	0	33.6	33.6																									
14	0	0	18.7	18.7																									
16	0	0	15.1	15.1																									
18	0	0	20.3	15.0																									
20	0	0	7.5	9.5																									
22	0	0	7.1	8.2																									
24	0	0	7.1	8.2																									
26	0	0	6.5	6.1																									
28	0	0	6.1	6.1																									
30	0	0	6.1	6.1																									
32	0	0	5.7	5.7																									
34	0	0	5.7	5.7																									
36	0	0	5.7	5.7																									
38	0	0	5.7	5.7																									
40	0	0	5.7	5.7																									
42	0	0	5.7	5.7																									
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108	0	0	5.7	5.7																									
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is irreversible and predicted that the hydroxyl group is essential to the structure.

Since this compound can exist with or without the water of hydration, the occupancy of the oxygen sites corresponding to the water molecules was investigated during the last least-squares refinement of the structure. It was found for the crystal under study that both oxygen atoms had full occupancy within the experimental errors.

The average interatomic distances are:

$$\begin{aligned} \text{K-O (eightfold coordination)} &= 2.805 \text{ \AA} \\ \text{B-O (threefold coordination)} &= 1.370 \text{ \AA} \\ \text{B-O (fourfold coordination)} &= 1.483 \text{ \AA} \\ \text{H-O} &= 0.96 \text{ \AA} \\ \text{H} \cdots \text{O} &= 2.18 \text{ \AA} \end{aligned}$$

However, it can be seen from Table 4, where the individual bond lengths are reported, that there are appreciable variations from the average, indicating that the potassium-oxygen and the boron-oxygen polyhedra are somewhat distorted.

The two potassium atoms are each surrounded by an 8-oxygen polyhedron. The average K-O distance of 2.805 Å is smaller than the average value of 2.903 Å found in $\text{K}[\text{B}_5\text{O}_8(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (Zachariasen & Plettinger, 1963) where the potassium atoms have also coordination number 8. This difference can be explained by the fact that $\text{K}_2[\text{B}_5\text{O}_8(\text{OH})] \cdot 2\text{H}_2\text{O}$ can exist with or without the two molecules of water. In the anhydrous compound the coordination number of the potassium atoms is 6 and 7 for K(1) and K(2), respectively. The average K-O distance in the hydrated

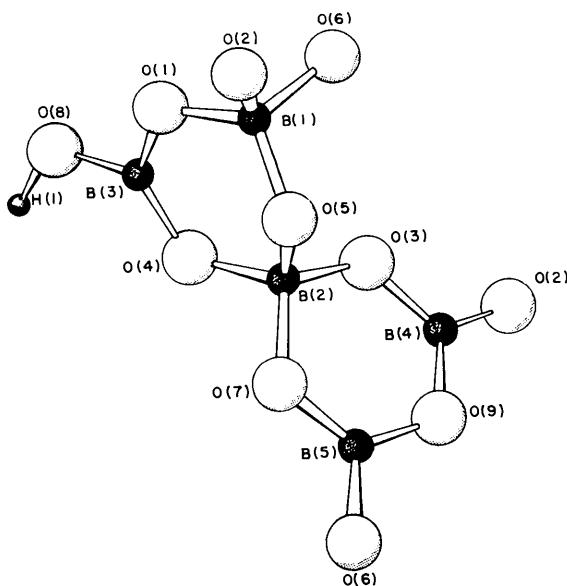


Fig. 2. The projection of the unit $[\text{B}_5\text{O}_8(\text{OH})]^{2-}$ on the (101) plane; these units are linked together to form a three-dimensional network.

compound must be a smaller value than would be expected for a typical 8-coordinated potassium, otherwise after dehydration the average K-O distances in the anhydrous compound would be too large for 6- and 7-coordinated potassium atoms. In dehydration processes where the structure remains the same, only a slight rearrangement of atoms takes place.

The average B-O distances are in good agreement with the corresponding distances found in other borates.

The dimensions found for the hydrogen bond corresponding to the hydroxyl group are:

$$\begin{aligned} \text{O(8)-H(1)} &= 0.84 \pm 0.21 \text{ \AA} & \text{O(8)-O(5)} &= 2.740 \pm 0.005 \text{ \AA} \\ \text{O(5)} \cdots \text{H(1)} &= 1.94 \pm 0.21 \text{ \AA} \end{aligned}$$

The dimensions found for the hydrogen bonds corresponding to the two water molecules are:

$$\begin{aligned} \text{O(10)-H(2)} &= 0.84 \text{ \AA} & \text{H(2)} \cdots \text{O(1)} &= 2.03 \text{ \AA} \\ \text{O(10)-H(3)} &= 1.02 \text{ \AA} & \text{H(3)} \cdots \text{O(3)} &= 2.25 \text{ \AA} \\ & & \text{H(3)} \cdots \text{O(4)} &= 2.23 \text{ \AA} \end{aligned}$$

$$\begin{aligned} \text{O(10)-O(1)} &= 2.810 \text{ \AA} \\ \text{O(10)-O(3)} &= 3.073 \text{ \AA} \\ \text{O(10)-O(4)} &= 3.013 \text{ \AA} \\ \text{H(2)-O(10)-H(3)} &= 91.0^\circ \end{aligned}$$

$$\begin{aligned} \text{O(11)-H(4)} &= 0.90 \text{ \AA} & \text{H(4)} \cdots \text{O(9)} &= 2.29 \text{ \AA} \\ \text{O(11)-H(5)} &= 1.21 \text{ \AA} & \text{H(5)} \cdots \text{O(10)} &= 2.39 \text{ \AA} \end{aligned}$$

$$\begin{aligned} \text{O(11)-H(4)} \cdots \text{O(9)} &= 3.06 \text{ \AA} \\ \text{O(11)-H(5)} \cdots \text{O(10)} &= 3.02 \text{ \AA} \\ \text{H(4)-O(11)-H(5)} &= 106.5^\circ \end{aligned}$$

The large values for the $\text{H} \cdots \text{O}$ bonds can be interpreted as a consequence of the zeolitical nature of the hydration water of this compound. A small strength must be attached to these bonds so that it would be easy for the compound to lose its water of hydration. Note that the water H(2)-O(10)-H(3) forms one of its hydrogen bond with two oxygens O(3) and O(4).

With the exception of the O(3) and O(4) all the oxygens of the unit $[\text{B}_5\text{O}_8(\text{OH})]^{2-}$ form four bonds. Instead, O(3) and O(4) form three bonds, one K-O, one B-O (triangle) and one B-O (tetrahedral). However, they also form weak hydrogen bonds with the water molecule O(10). The three bonds which O(3) forms with K(2), B(2), and B(4) are the same in length to the three bonds which O(4) forms with K(1), B(2), and B(3), respectively.

Because of the long $\text{H} \cdots \text{O}$ bonds of the water molecules, the large uncertainty in the positions of the hydrogen atoms, and the short K-O distances, it is not possible to make a quantitative valence balance for $\text{K}_2[\text{B}_5\text{O}_8(\text{OH})] \cdot 2\text{H}_2\text{O}$. However, it can be seen from Table 4 that all the distortions are in the right direction. For instance, from its coordination O(5) seems underbonded, but as one would expect the B-O(5) distances are significantly smaller than the

average B–O for tetrahedral coordination. Furthermore, the balance for O(2), O(6), O(7), which do not form any hydrogen bonds, is exactly 2 if one assigns a strength of $\frac{1}{3}$ to each K–O bond, 1 to each triangular B–O bond, and $\frac{2}{3}$ to each tetrahedral B–O bond.

The anisotropic thermal coefficients β_{ij} of Table 2 were used to compute (Busing, Martin & Levy, 1964) the root mean square displacements along principal axes, together with the angles that the principal axes

form with the vectors **a**, **b**, and **c** of the crystal. These values are reported in Table 5.

Although a detailed analysis of the data of Table 5 will not be presented, qualitatively these data reveal many features of physical interest. For instance, the water oxygens have larger thermal amplitudes than the hydroxyl oxygen, which in turn has larger displacements than the oxygen atoms. The thermal motion of the water oxygen O(11) is much larger than the water

Table 5. *Magnitudes and orientation of thermal ellipsoids*

	<i>i</i>	r.m.s. amplitudes	Angles with respect to		
			<i>a</i>	<i>b</i>	<i>c</i>
K(1)	1	0.118 (2) Å	157 (3)°	109 (4)°	103 (1)°
	2	0.139 (2)	106 (4)	20 (4)	101 (2)
	3	0.194 (2)	74 (1)	96 (1)	163 (1)
K(2)	1	0.105 (2)	80 (1)	66 (10)	154 (10)
	2	0.112 (2)	85 (2)	24 (10)	65 (10)
	3	0.218 (2)	169 (1)	81 (1)	97 (1)
B(1)	1	0.08 (1)	103 (33)	47 (40)	134 (53)
	2	0.09 (1)	121 (20)	58 (46)	48 (54)
	3	0.11 (1)	146 (13)	121 (12)	104 (13)
B(2)	1	0.07 (1)	86 (14)	41 (53)	130 (53)
	2	0.08 (1)	100 (13)	48 (53)	43 (53)
	3	0.11 (1)	169 (13)	93 (11)	100 (12)
B(3)	1	0.07 (1)	138 (13)	66 (15)	59 (5)
	2	0.10 (1)	59 (15)	32 (14)	85 (10)
	3	0.15 (1)	113 (6)	70 (7)	148 (5)
B(4)	1	0.09 (1)	76 (35)	154 (45)	68 (34)
	2	0.10 (1)	48 (34)	165 (47)	52 (35)
	3	0.11 (1)	135 (30)	84 (23)	45 (29)
B(5)	1	0.07 (1)	65 (8)	58 (10)	138 (11)
	2	0.10 (1)	75 (16)	44 (15)	50 (12)
	3	0.14 (1)	151 (11)	62 (14)	99 (13)
O(1)	1	0.100 (7)	115 (48)	140 (35)	119 (5)
	2	0.105 (6)	27 (46)	117 (42)	92 (24)
	3	0.155 (5)	79 (5)	63 (4)	150 (4)
O(2)	1	0.059 (8)	75 (4)	99 (5)	162 (6)
	2	0.108 (6)	110 (7)	24 (6)	104 (6)
	3	0.143 (5)	154 (6)	113 (7)	100 (4)
O(3)	1	0.078 (7)	91 (6)	82 (24)	172 (24)
	2	0.090 (6)	102 (3)	13 (13)	82 (25)
	3	0.163 (5)	168 (3)	102 (3)	91 (3)
O(4)	1	0.088 (8)	129 (12)	47 (8)	68 (6)
	2	0.112 (7)	39 (12)	60 (10)	67 (7)
	3	0.159 (5)	85 (5)	57 (4)	147 (4)
O(5)	1	0.088 (6)	67 (13)	152 (11)	106 (14)
	2	0.104 (5)	47 (30)	85 (28)	43 (32)
	3	0.111 (6)	128 (30)	118 (11)	51 (32)
O(6)	1	0.076 (7)	91 (5)	49 (13)	138 (13)
	2	0.096 (6)	85 (6)	41 (13)	49 (13)
	3	0.137 (5)	174 (6)	86 (5)	86 (6)
O(7)	1	0.085 (7)	101 (16)	35 (38)	123 (33)
	2	0.091 (7)	68 (10)	55 (38)	43 (30)
	3	0.127 (5)	155 (7)	87 (6)	65 (7)
O(8)	1	0.107 (7)	158 (27)	106 (25)	75 (11)
	2	0.119 (7)	111 (28)	31 (15)	112 (8)
	3	0.265 (7)	96 (2)	116 (2)	153 (2)
O(9)	1	0.081 (7)	102 (8)	79 (16)	163 (6)
	2	0.099 (7)	66 (4)	24 (9)	84 (16)
	3	0.196 (5)	152 (2)	69 (2)	74 (2)
O(10)	1	0.142 (8)	120 (4)	101 (6)	147 (3)
	2	0.200 (8)	57 (7)	146 (7)	97 (6)
	3	0.247 (8)	132 (5)	121 (7)	58 (3)
O(11)	1	0.211 (11)	76 (13)	67 (3)	153 (8)
	2	0.249 (10)	16 (11)	88 (6)	73 (12)
	3	0.410 (12)	82 (3)	157 (2)	112 (2)

oxygen O(10). This is due to the fact that O(11) forms only two bonds with the rest of the structure whereas O(10) forms four bonds. The oxygen O(5), which is bonded to two tetrahedrally coordinated boron atoms, has the smallest anisotropy of thermal motion among the oxygen atoms.

Furthermore, the directions of maximum displacement observed for the atoms O(6), O(7), O(9), which form a triangle around B(5), are nearly parallel to the normal of the plane formed by the three atoms. The same is true for the atoms O(1), O(4), O(8) which form the triangle around B(3).

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The Structure of Dichlorobis-(2-methylpyridine)copper(II): A Five-Coordinate Copper Complex

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Dichlorobis-(2-methylpyridine)copper(II) crystallizes in the triclinic system, space group $P\bar{1}$, with lattice constants $a = 8.58 \pm 0.05$, $b = 9.20 \pm 0.05$, $c = 10.99 \pm 0.05$ Å, $\alpha = 86.8 \pm 0.5^\circ$, $\beta = 110.1 \pm 0.05^\circ$ and $\gamma = 123 \pm 1^\circ$. The structure was determined by the heavy-atom method and refined by least-squares analysis to a final R value of 0.11 for 1152 visually estimated intensities. Each copper atom is surrounded by two chlorine and two nitrogen atoms in an approximately square-planar arrangement. The 2-methylpyridine ligands lie approximately in a plane which is perpendicular to the square-coordination plane and the methyl groups are in a *cis* arrangement, effectively hindering any close approach by the chlorine atom of another molecule at one axial coordinating site. There is evidence of some intermolecular association at the other axial site through Cu-Cl bridging, so that the environment of each copper atom may be described as a tetragonal pyramid.

Introduction

Metal halide complexes with pyridine and methylpyridines have been the subject of study for many years. More recently Graddon, Schulz, Watton & Weeden (1963) and Graddon & Watton (1965) have studied some metal halide complexes with 4-methylpyridine and 2-methylpyridine. Whilst they found that the properties of these complexes of cobalt(II) and copper(II) with 4-methylpyridine were substantially the same as those with the analogous pyridine complexes, they observed that the presence of 2-methylpyridine in these types of complexes could provide steric hindrance to

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octahedral coordination. Thus they could not prepare a 2-methylpyridine complex with cobalt(II) which corresponded to the octahedral $\text{CoCl}_2(\text{pyridine})_2$ form (Mellor & Coryell, 1938; Dunitz, 1957). Only a blue tetrahedral form was isolated. The complexes with copper(II) of the form $\text{CuX}_2(2\text{-methylpyridine})_2$ (where X is Cl or Br) were found to have properties which did not correspond to those of the analogous compounds of pyridine and 4-methylpyridine. The colours of the 2-methylpyridine complexes were much deeper and there were differences observed in the solid state visible absorption spectra which indicated a change in the stereochemistry of the copper atom.

On the basis of this evidence, Graddon & Watton (1965) postulated square-planar monomeric structures for these 2-methylpyridine complexes, in which the